THE EFFECT OF SUPERCRITICAL WATER ON VITRINITE REFLECTANCE AS OBSERVED IN CONTACT METAMORPHISM AND PYROLYSIS EXPERIMENTS

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Introduction

Natural thermal maturation of sedimentary organic matter (SOM), which includes both coal and dispersed organic matter, increases with heating. In particular, dike contact metamorphic zones are widely studied because within the narrow sampling range near the dike, SOM composition changes little along a well-exposed sample plane while thermal maturation increases markedly as temperature increases from ambient to as high as 700°C (Bostick, 1979; Clayton and Bostick, 1986; Bishop and Abbott, 1994; Galushkin, 1997, and Barker et al., 1998; among others). These studies indicate contact metamorphism typically increases thermal maturity as measured by vitrinite reflectance, Rock-Eval parameters, as well as affecting SOM, petroleum and biomarker compositions. In this study, mean vitrinite reflectance in oil (mean or maximum parameter both annotated as R_o for this general discussion) is used because it is widely reported in dike studies as an index of heating relative to petroleum generation (i.e., the thermal maturation process). R_o is a physical measure of the degree of aromaticity in the SOM. During thermal maturation, the degree of aromaticity in vitrinite increases with the continuing condensation of aromatic clusters (van Krevelen, 1981; Wilson, 1987).

Given the change in host-rock temperature from ambient to those produced by contact with a magma, a surprising aspect of these studies is that R_o *does not always* continue to increase as a dike is closely approached. Next to some dikes R_o increase is retarded or R_o may even decrease. This is true whether R_o is measured next to dikes as discussed above or next to sills as well as whether maximum or random reflectance of vitrinite is measured (Raymond and Murchison, 1989). Fluid inclusion evidence indicates that the zone of retarded or reduced R_o roughly corresponds to a zone where water vapor or supercritical-water phases evolve during contact metamorphism by the dike (Barker, 1995). In particular, the limited range of physical and chemical conditions that lead to the evolution of supercritical fluids may explain the retarded or reduced R_o found near dikes. The development of water vapor is thought less important because it typically forms during contact metamorphism (Jaeger, 1959; Delaney, 1982; 1987) at the shallow to moderate crustal depths prevalent in sedimentary basins and its effects should be widely expressed next to dikes. Although there are other possible causes of retarded or reduced R_o near dike contacts, the purpose of this paper is to investigate the effect of supercritical water on thermal maturation by hydrous pyrolysis experiments.

Contact Metamorphism

The sample selected for hydrous pyrolysis study is a bituminous coal (mean random R_o = 0.6 %), taken from a site not locally affected by contact metamorphism even though from an area where a mid-Cretaceous age dike swarm intrudes the Upper Jurassic-Lower Cretaceous Strzelecki Group, western onshore Gippsland Basin, Victoria, Australia. This sample was collected about 50 meters below the surface in the State coal mine near Wonthaggi, Victoria. The Strzelecki Group banded coals contain mostly normal vitrinite (i.e., not suppressible by the definition of Barker et al., 1996). Thermal history reconstruction suggests that at the time of dike swarm intrusion the host rock was at a temperature of 100-135°C while fracture-bound fluid inclusions in the host rocks next to thin dikes (< 3.4 m thick) suggest temperature increases to at least 450°C at the dike contact (Fig. 1). Burial history reconstruction indicates that when intrusion occurred the host rocks were near two km depth and at about 20 MPa pressure using a fresh water hydrostatic gradient (Barker et al., 1998). Fresh water boils at about 300°C at this depth. The critical point of fresh water is near 374°C, 22 MPa. Thus, the temperature and pressure near the dike contact, along with the low to moderate salinity fluids (Barker, 1995) are conditions close to those required for the development of water vapor or supercritical fluids (Roedder, 1984; Bodnar and Vityk, 1994).

Pyrolysis Experiments

The development of supercritical fluids next to these dikes was simulated by heating aliquots of the Strzelecki Group coal in closed-system experiments using pyrolysis techniques developed by Lewan (1993) and a small stainless steel reactor described by Barker et al. (1996). The initial series of pyrolysis experiments was held at temperatures of 300°C, 330°C, 365°C and 380°C for 72 hours. The 380°C experiment was then run again for 24 hours. Experiments at 365°C or lower temperature were designed to keep liquid water in contact with the sample. Experiments at 380°C introduced supercritical water to the sample.

These experiments showed an increase in vitrinite reflectance as long as pyrolysis temperatures were held to subcritical liquid-water conditions. The runs at 380°C, with supercritical-water conditions in contact with the sample, showed a reduced R_o (Fig. 2). Increasing time from 24 to 72 hours at 380°C produced a further reduction in R_o.

Discussion

During contact metamorphism R_o increase sometimes is retarded or even reduced close to the dike contact, even though fluid inclusion homogenization data indicates that temperatures were still increasing. Fluid inclusion evidence also indicates that the evolution of water vapor or supercritical water in the rock pores roughly corresponds to the zone where R_o is retarded or reduced. This relationship infers that the generation of water vapor or supercritical water near the dike contact may change vitrinite evolution reactions. The limited range of conditions in sedimentary basins that allow supercritical fluids to exist may explain why a retarded or reduced R_o is not always observed near dikes. Because water vapor and supercritical water have a limited range of occurrence in sedimentary basins, there may be other causes of retarded or reduced R_o next to dikes. Some of these causes are hydrothermal overpressuring next to the dike, catalytic effects, advection, convection, groundwater flow across the dike, and the presence of suppressible SOM.

The physical and chemical basis for a retarded R_o with increasing temperature remains speculative. For example, is it that condensation reactions in SOM are inhibited causing a retardation of R_o or is condensation destroyed causing a reduction of R_o. What is known is that within the zone of retarded or reduced R_o, molecular disorder is increasing (Khavari-Khorasani et al., 1990); and the fraction of aromatic carbon increases and then may fluctuate (Barker, 1995). Further, as the dike is approached, ^{13}C CP MAS nuclear magnetic resonance (NMR) data suggest that phenol and carbonyl contents initially decrease but that there is slight increase in phenol and carbonyl content in the zone of retarded R_o (Barker, 1995). Along with these changes, the total organic carbon (TOC) content is lowered (Degens, 1965; Barker, 1995). The loss in TOC as the dike is approached is partially attributable to petroleum generation and migration as shown by a corresponding decrease in Rock-Eval hydrogen index (HI) and S_1 (Fig. 3). Next to some dikes, HI and the oxygen index (OI) may both stop decreasing or start to increase in the zone where R_o increase is retarded. This change in HI and OI may be caused by the addition of phenol and carbonyl radicals to the residual SOM. These geochemical data suggest that in the presence of water vapor or supercritical water, hydrogen and oxygen are being introduced into the coal during reactions like those observed in liquid-water pyrolysis experiments (Stalker et al., 1994; Lewan, 1997).

A fraction of the TOC, however, also appears to directly react with the pore water and is in part mobilized as CO_2 (Lewan, 1992; Price, 1994). Given the exceptional solubility of SOM in supercritical fluids, SOM may be directly dissolved in the supercritical water (Lewan, 1993). The strong loss of TOC indicates the presence of a supercritical fluid rather than a vapor phase. SOM is thought to have a far lower solubility in a water vapor. A mesh-like porous structure observed in the Strzelecki Group vitrinite after supercritical pyrolysis also may be a reflection of a selective dissolution process.

Conclusions

1. The evidence suggests several reaction mechanisms producing a reduction or a retardation of condensation in SOM caused by the development of water vapor or supercritical water: a) After high temperature condensation reactions, the substitution of oxygen- and hydrogen-bearing radicals destroy aromatic carbon bonds in the highly condensed SOM; b) further condensation of the SOM may be retarded by the early reaction of phenolic and carbonyl radicals with the aromatic carbon clusters in a less mature vitrinite; and c) simultaneous thermal maturation and dissolution of the condensed structures at the surface of the vitrinite leaving residual SOM with a retarded aromaticity.
2. Experimental, geochemical and petrographic evidence indicate direct SOM reactions with water are a major factor during contact metamorphism near the dike contact.
3. The atypical occurrence of retarded R_o near dike contacts is attributed to the limited range of physical conditions and pore-water chemistry under which supercritical water can exist in sedimentary basins.
4. Because water vapor and supercritical fluids have a limited range of occurrence, there may be other causes of retarded or reduced R_o next to dikes in sedimentary basins.

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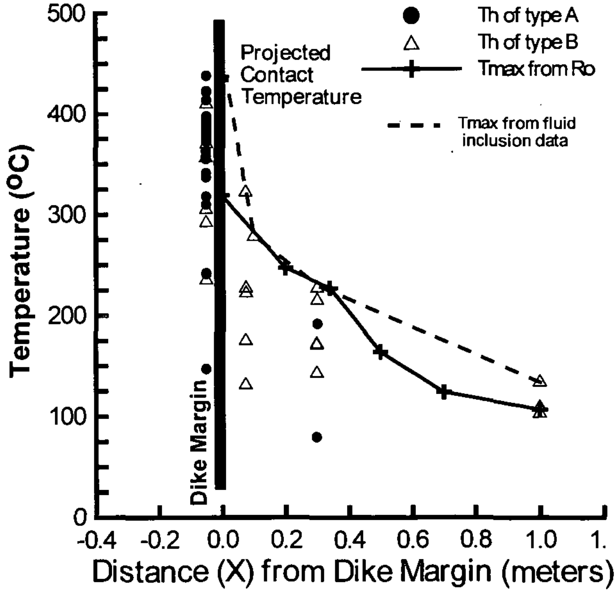

Figure 1. Measurements and calculated maximum host rock temperatures reached next to the 0.6 m thick San Remo-1 dike, western onshore Gippsland Basin, Australia. Figure from Barker (1995). T_h = homogenization temperature of a fluid inclusion. Type A and B refer to types of fracture-bound fluid inclusions. Projected contact temperature is estimated from fluid inclusion measurements on a host rock xenolith partially imbedded in the dike. T_{max} from Ro refers to a temperature estimate made using the hydrothermal geothermometer of Barker and Pawlewicz (1994). A reassessment of the position of the xenolith sample used to determine the projected contact temperature indicates it was taken a few centimeters from the dike contact rather than 20 cm away as reported by Barker (1995).

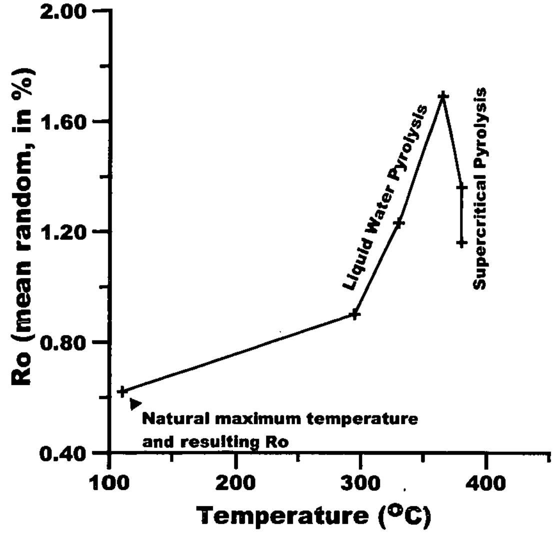

Figure 2. Vitrinite reflectance of Strzelecki Group coal after natural diagenesis, liquid water and supercritical water pyrolysis.

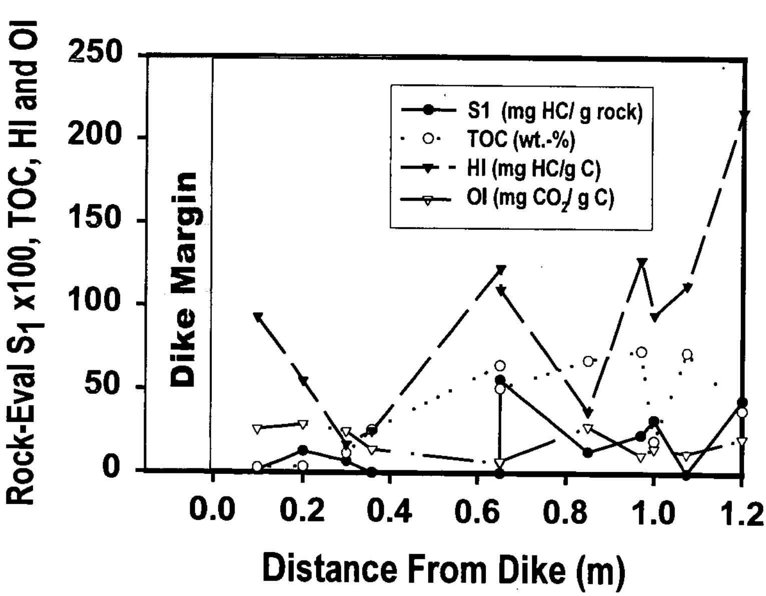

Figure 3. Rock-Eval pyrolysis assay results from coaly rocks in the Strzelecki Group next to the San Remo-1 dike, western onshore Gippsland basin, Australia. Data from Barker (1995)